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ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED COMPOUNDS

A New Method for the Synthesis of Beta-Ketophosphonic and Unsaturated Alpha-Hydroxyphosphonic Esters

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Acad A. Ye. Arbuzov
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/This is another report on results of the extensive investigation on organic phosphorus compounds which is being carried out at several institutes in Kazan'. The work referred to here has CW implications, because compounds having cholinesterase inhibitor activity as well as products which are closely related to this class of compounds are being synthesized in the course of the investigation in question./

The classical method for the synthesis of esters of phosphonic acids is at present the method of A. Ye. Arbuzov, proposed by him in 1905, and consisting in the interaction of halogen-containing organic compounds with full esters of phosphorous acids (1).

Also of considerable preparative importance for obtaining esters of phosphonic acids is the method of their synthesis from various halogenated derivatives and salts of dialkylphosphorous acids which was proposed by Miechaelis and Becker (2) and successfully applied subsequently by Nylen (3), A. Ye. Arbuzov, B. A. Arbuzov (4), and others.

In 1947, during the study of the action of salts of dialkylphosphorous acids on isomeric halogenated allylic compounds, I found (5) that dialkylphosphorous acids in the presence of an alkaline catalyst are capable of addition to the double bond of unsaturated phosphonic esters. This observation subsequently became the basis for the development of a new method for the synthesis of esters of phosphonic acids by addition of dialkylphosphorous acids in the presence of alcoholates of alkaline metals to different alpha, beta-unsaturated electrophylic compounds: unsaturated nitrites, ketones, esters of acids, aldehydes, and certain other reagents.

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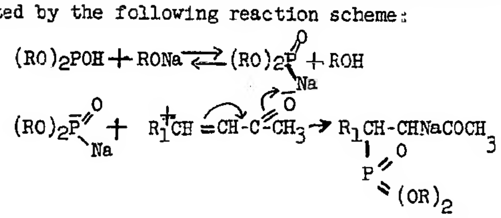
In the preceding work the addition of dialkylphosphorous acids to beta, beta-dimethyldvinyl ketone, the nitrile of acrylic acid, and methylacrylate was described (6).

It was shown that beta, beta-dimethyldivinyl ketone adds dialkylphosphorous acids (first molecule) at the unsubstituted vinyl group; the ability for addition of the substituted vinyl group is considerably decreased in it. In the course of the above-mentioned work it was extremely interesting to study the addition of dialkylphosphorous acids to the simplest alpha, beta-unsaturated ketones with the vinyl groups replaced in different positions, in a different degree, and with different radicals.

As objects of study in the present investigation ethylidenacetone, benzalacetone, and furfuralacetone were taken. Products of addition were obtained with 70-80% yields in the majority of cases. It appeared that ethylidenacetone, furfuralacetone, and benzalacetone add to dialkylphosphorous acids at the double bond.

The constants of the beta-phosphonic esters obtained are cited in Table 1.

Of all the ketones mentioned above, ethylidenacetone adds to dialkylphosphorous acids most vigorously, benzal acetone less vigorously, and, least energetically furfuralacetone. The mechanism of addition reactions can be represented by the following reaction scheme:



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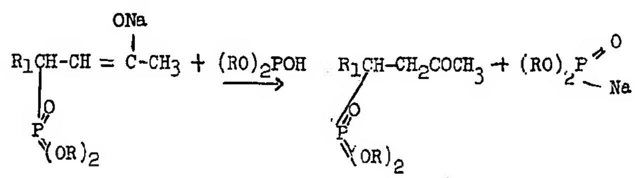
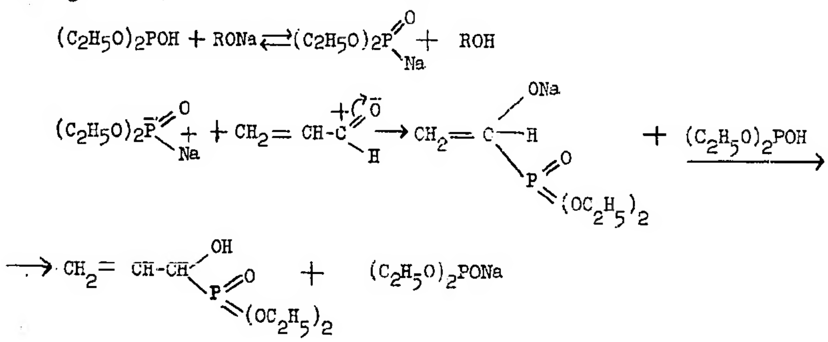


In the course of work on the addition of dialkylphosphorous acids to the simplest unsaturated ketones, I further studied the reactions of addition of dialkylphosphorous acids to ketones with two substituents in the vinyl group, namely mesityl oxide and different unsaturated aldehydes. The reactions were carried out by the same method as that applied with the simplest unsaturated ketones, i.e. in the presence of alcoholates of alkaline metals.

This year, V. S. Abramov (7) showed that sodium dialkylphosphite under ordinary conditions and dialkylphosphorous acids in the presence of alcoholates of alkaline metals add to the carbonyl group of saturated aldehydes and ketones; he carried out the reaction according to the method which I developed for adding dialkylphosphorous acids to different unsaturated electrophylic reagents. The dialkylphosphorous acids to different unsaturated electrophylic reagents. The addition of sodium diethylphosphite to the carbonyl group of alpha-keto-phosphonic esters was first demonstrated by A. Ye. Arbuzov and M. M. Azanovskaya (8) on the example of the reaction between acetyl chloride and sodium diethylphosphite.

As a result of the study of the products which I obtained by the addition of dialkylphosphorous acids to mesityl oxide and unsaturated aldehydes, it was established that they produce no characteristic reactions for the aldehyde group but produced a positive reaction for the hydroxyl group; the latter group was subsequently determined quantitatively according to Tserevitinov for certain of the products obtained. On the basis of the data obtained the conclusion was reached that all products obtained from the addition of dialkylphosphorous acids to unsaturated aldehydes and mesityl oxide (see Table 2) are alpha-hydroxyphosphonic esters and that, consequently, the addition of dialkylphosphorous acids to unsaturated aldehydes and mesityl oxide takes place at the carbonyl group, and not at the hydrocarbon double bond.

The formation of alpha-oxyphosphonic esters can be represented by the following scheme:



Work is being continued with the aim of a more profound and broader study of the reactions of addition of dialkylphosphorous acids to electrophylic reagents.

In conclusion I consider it my pleasant duty to express thanks to my teacher B. A. Arbuzov, Corresponding Member Acad Sci USSR, for his attention toward and interest in the work I carried out.

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Presented 29 April 1950

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/Tables 1 and 2 follow./

Table 1

Formula	Boiling Point in °C/mm Hg	n_D^{20}	d_4^{20}
$CH_3\text{-}CO\text{-}CH_2\text{-}CH(CH_3)P(=O)(OCH_3)_2$	134-135/10	1.4411	1.1313
$CH_3CO\text{-}CH_2CH(CH_3)P(=O)(OC_2H_5)_2$	139-140/10	1.4387	1.0850
$CH_3CO\text{-}CH_2CH(CH_3)P(=O)(OC_4H_9iso)_2$	156-158/10	1.4400	1.0221
$CH_3CO\text{-}CH_2CH(CH_3)P(=O)(OC_4H_9n)_2$	172-173/10	1.4412	0.9985
$CH_3CO\text{-}CH_2CH(C_6H_5)P(=O)(OCH_3)_2$	189-190/10	1.5095	1.1791
$CH_3CO\text{-}CH_2CH(C_6H_5)P(=O)(OC_2H_5)_2$	203/16	1.5050	1.1309
$CH_3CO\text{-}CH_2CH(C_6H_5)P(=O)(OC_4H_9iso)_2$	208/12	1.4900	1.0736
$CH_3CO\text{-}CH_2CH(C_6H_5)P(=O)(OC_4H_9n)_2$	219-220/13	1.4927	1.0737
$CH_3CO\text{-}CH_2CH(C_4H_3O)P(=O)(OCH_3)_2$	163-164/6	1.4835	1.2181
$CH_3CO\text{-}CH_2CH(C_4H_3O)P(=O)(OC_2H_5)_2$	192-193/16	1.4755	1.1616
$CH_3CO\text{-}CH_2CH(C_4H_3O)P(=O)(OC_4H_9iso)_2$	161/3	1.4711	1.0932
$CH_3CO\text{-}CH_2CH(C_4H_3O)P(=O)(OC_4H_9n)_2$	182/4	1.4730	1.0995

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Table 2

Formula	Boiling Point in °C/mm Hg	Melting Point in °C	n_D^{20}	d_4^{20}
$(CH_3)_2C{=}CH{-}C(CH_3)(OH)P(O)(OCH_3)_2$	136/12	--	1.4457	1.1263
$(CH_3)_2C{=}CH{-}C(CH_3)(OH)P(O)(OC_2H_5)_2$	138/11	--	1.4400	1.0675
$(CH_3)_2C{=}CH{-}C(CH_3)(OH)P(O)(OC_4H_9iso)_2$	162-163/12	--	1.4409	1.0029
$(CH_3)_2C{=}CH{-}C(CH_3)(OH)P(O)(OC_4H_9n)_2$	171-172/13	--	1.4440	1.0084
$CH_2{=}CH{-}CH(OH)P(O)(OCH_3)_2$	149-151/10	--	1.4575	1.2188
$CH_2{=}CH{-}CH(OH)P(O)(OC_2H_5)_2$	154-155/10	--	1.4506	1.1225
$CH_2\ CH{-}CH(OH)P(O)(OC_3H_7iso)_2$	140-141/7	--	1.4415	1.0465
$CH_2{=}CH{-}CH(OH)P(O)(OC_4H_9iso)_2$	166-170/10	--	1.4411	1.0130
$CH_2{=}CH{-}CH(OH)P(O)(OC_4H_9n)_2$	168-170/10	--	1.4348	0.9968
$CH_3{-}CH{=}CH{-}CH(OH)P(O)(OCH_3)_2$	150-152/8	--	1.4630	1.1690
$CH_3{-}CH{=}CH{-}CH(OH)P(O)(OC_2H_5)_2$	163-164/9	--	1.4555	1.1005
$C_4H_3O{-}CH{=}CH{-}CH(OH)P(O)(OC_2H_5)_2$	--	106-107		
$C_6H_5CH{=}CH{-}CH(OH)P(O)(OCH_3)_2$	--	101-102		
$C_6H_5CH{=}CH{-}CH(OH)P(O)(OC_2H_5)_2$	--	104-105		

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